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# Canadian Journal of Research

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JANUARY, 1943

NUMBER 1

## THE RESONANCE METHOD OF MEASURING THE RATIO OF THE SPECIFIC HEATS OF A GAS, $C_p/C_v$

### PART IV<sup>1</sup>

BY A. L. CLARK<sup>2</sup> AND L. KATZ<sup>3</sup>

### Abstract

This paper is a continuation of the work already published in three parts in this Journal (1, 2). In it a new theoretical treatment of the effect of the non-adiabatic behaviour of a gas subjected to alternate compressions and rarefactions is developed for both spherical and cylindrical chambers. This theory is then applied to the previous results as well as to some new ones. It is believed now that the results are as accurate as may be obtained by direct experimental methods, under the most favourable conditions.

### Introduction

The resonance method of measuring the ratio of the specific heats of certain gases was described by the authors in Parts I and II, and results were given. Experiments on other gases were described in Part III. At the time of publication of Parts I and II the authors had not been able completely to solve an equation used in calculating the effect of heat conduction between the gas and the walls of the container. This effect causes the gas to depart from the true adiabatic behaviour. An approximate solution was found and the results published in Parts I and II were based on this method.

This equation has since been solved mainly through the efforts of the junior author. In fact, the results of Part III were in the hands of the printer when the difficulties were finally overcome, and the results for sulphur dioxide and nitrous oxide, which had been calculated by the older method, were corrected in proof by use of the new solution.

In this fourth paper the new treatment is given in detail and recalculations of some results are also given. Fortunately the results obtained by the more rigorous treatment differ only slightly from the older results, and then only for the more highly conducting gases—hydrogen and helium. It was deemed wise to experiment on these gases at considerably higher pressures than were applied in the earlier work, in order to have more data for the setting up of the empirical equation connecting the value of the ratio  $\gamma$  and the pressure.

<sup>1</sup> Manuscript received July 27, 1942.

Contribution from the Department of Physics, Queen's University, Kingston, Ont.

<sup>2</sup> Professor of Physics.

<sup>3</sup> At the time, holder of a Studentship under the National Research Council of Canada. At present, candidate for the degree of Doctor of Philosophy, California Institute of Technology, Pasadena, Calif.

This empirical equation enables one to calculate very accurately the value of  $\gamma$  in the low pressure region—just where the experimental results are most unsatisfactory. The pressures for hydrogen and helium were extended to about 60 atm.

### The Fundamental Equation for the Mean Instantaneous Pressure

The motion of the piston is maintained by the actuating coils and is assumed to be simple harmonic. The amplitude of the motion is so small (0.07 cm.) that the changes in pressure, temperature, and volume are all very small, so that this assumption is valid. The motion of the piston may be represented by

$$x = x_1 \cos \omega t, \quad (1)$$

where  $x_1$  is the maximum displacement.

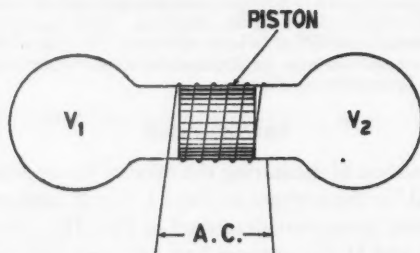


FIG. 1. Simple diagrammatic sketch of apparatus.

The moving piston alternately compresses and expands the enclosed gas, and by changing the frequency of the current in the actuating coils it is possible to obtain resonance for the piston motion. The reaction of the compressed gas on the piston, Fig. 1, is given by  $(P_2 - P_1)$  per unit area of piston surface. We may write

$$(P_2 - P_1) = (P_2 - P_0) + (P_0 - P_1),$$

but from the symmetry of the arrangement  $(P_2 - P_0) = -(P_0 - P_1) = (P - P_0)$ , where  $P$  refers to either one of the two values. So

$$(P_2 - P_1) = 2(P - P_0). \quad (2)$$

The instantaneous values of the pressure, temperature, and specific volume may be written

$$\begin{aligned} P &= P_0 + P' \cos(\omega t + \delta_1) \quad (a) \\ T &= T_0 + T' \cos(\omega t + \delta_2) \quad (b) \\ v &= v_0 + v' \cos(\omega t + \delta_3). \quad (c) \end{aligned} \quad (3)$$

The changes in  $P$ ,  $T$ , and  $v$  are not necessarily in phase with the displacement  $x$ , nor with one another. Undoubtedly the flow of heat from point to point will change the phase relations.

It will be convenient to replace Equations (3) by the corresponding exponentials. The displacement, pressure, temperature, and specific volume

become the real parts of the corresponding complex quantities, so we may write

$$\begin{aligned}x &= x_1 e^{i\omega t} & (a) \\P &= P_0 + P_1 e^{i\omega t} & (b) \\T &= T_0 + T_1 e^{i\omega t} & (c) \\v &= v_0 + v_1 e^{i\omega t} & (d)\end{aligned}\quad (4)$$

where  $P_1 = P' e^{i\omega t}$ ,  $T_1 = T' e^{i\omega t}$ , and  $v_1 = v' e^{i\omega t}$ .

Since the gas containers  $V_1$  and  $V_2$  (Fig. 1) are small compared to the wavelength of sound at the frequencies used and since pressure differences are equalized with the velocity of sound (much greater than the velocity of heat flow),  $P$  may be regarded as a function of time alone and not a function of position within  $V_1$  or  $V_2$ .  $T$  and  $v$  will vary however from point to point as well as with time. The same statements apply to the complex quantities  $P$ ,  $T$ , and  $v$ .

Now  $v$  and  $T$  may be taken as the independent variables, so that

$$\Delta P = \left( \frac{\partial P}{\partial v} \right)_T \Delta v + \left( \frac{\partial P}{\partial T} \right) \Delta T. \quad (5)$$

Since  $|P_1| \ll P_0$ , we have  $\left( \frac{\partial P}{\partial T} \right)_v \approx \left( \frac{\partial P_0}{\partial T_0} \right)_{v_0}$  and  $\left( \frac{\partial P}{\partial v} \right)_T \approx \left( \frac{\partial P_0}{\partial v_0} \right)_{T_0}$ . Both functions may be regarded as constant over the small range of pressure and temperature involved. Combining with Equations (4)

$$P_1 = \left( \frac{\partial P_0}{\partial T_0} \right)_{v_0} T_1 + \left( \frac{\partial P_0}{\partial v_0} \right) v_1. \quad (6)$$

From what has been said the average value of  $P_1$  may be found, i.e.,

$$\bar{P}_1 = (\bar{P} - P_0) = \left( \frac{1}{V} \int_V P dx dy dz - P_0 \right) = (P - P_0) = P_1.$$

$P_1$  in Equation (6) is most easily expressed in terms of  $\bar{T}_1$  and  $\bar{v}_1$ ; thus taking space average of Equation (6)

$$P_1 = \left( \frac{\partial P_0}{\partial T_0} \right)_{v_0} \bar{T}_1 + \left( \frac{\partial P_0}{\partial v_0} \right)_{T_1} \bar{v}_1. \quad (7)$$

The pressure acting per unit area of the piston is given by Equation (2) and may be taken as the real part of the following expression.

$$(P_2 - P_1) = 2(P - P_0) = 2P_1 e^{i\omega t} = 2 \left[ \left( \frac{\partial P_0}{\partial T_0} \right)_{v_0} \bar{T}_1 + \left( \frac{\partial P_0}{\partial v_0} \right)_{T_1} \bar{v}_1 \right] e^{i\omega t}. \quad (8)$$

#### The Specific Volume Change, $\bar{v}_1$

The total volume of the chamber at any instant is  $V = V_0 + ax$ , where  $V_0$  is the volume when the piston is at equilibrium and  $a$  is the area of the piston. Then if  $m_g$  is the mass of gas in the chamber, the mean specific volume is

$$\bar{v} = \frac{V}{m_g} = \frac{V_0}{m_g} \left( 1 + \frac{ax}{V_0} \right) = v_0 \left( 1 + \frac{ax}{V_0} \right).$$

Substituting for  $x$  from Equation (4a)

$$\bar{v}_1 e^{i\omega t} = (\bar{v} - v_0) = \frac{v_0 \alpha x}{V_0} = \frac{v_0}{V_0} \alpha x_1 e^{i\omega t} \quad (9)$$

### The Temperature Change, $\bar{T}_1$

With each compression the gas is heated and with each rarefaction it is cooled. Since the walls of the chamber are at constant temperature (or very nearly so) there will be transfers of heat between the gas and the walls, and consequently transfers from point to point within the gas. The temperature of the gas at any point then is modified and is not quite what it would be if the volume changes were perfectly adiabatic. The maximum change  $T_1$  at any point is modified as well, and necessarily also the mean value,  $\bar{T}_1$ . This effect is now to be incorporated.

From the first and second laws of thermodynamics

$$DQ = C_p dT - T_0 \left( \frac{\partial v_0}{\partial T_0} \right)_{P_0} dP,$$

and

$$C_p - C_v = T_0 \left( \frac{\partial P_0}{\partial T_0} \right)_{v_0} \left( \frac{\partial v_0}{\partial T_0} \right)_{P_0},$$

so

$$DQ = C_p \left( dT - \frac{\gamma - 1}{\gamma} \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} dP \right), \quad (10)$$

where

$$\gamma = C_p / C_v.$$

Combining Equations (4) and (10)

$$\frac{DQ}{dt} = C_p \left( T_1 - \frac{\gamma - 1}{\gamma} \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1 \right) i \omega e^{i\omega t}. \quad (11)$$

When there is loss of heat by conduction, the heat lost per unit mass per unit time is

$$\frac{DQ}{dt} = \frac{k}{\rho} \nabla^2 T,$$

where  $k$  is the conductivity and  $\rho = 1/v$ , the density of the gas.

Then, introducing Equation (4c),

$$\frac{DQ}{dt} = \frac{k}{\rho} \nabla^2 T_1 e^{i\omega t},$$

so

$$\nabla^2 T_1 = \frac{i \omega C_p \rho}{k} \left( T_1 - \frac{\gamma - 1}{\gamma} \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1 \right). \quad (12)$$

It is to be noted that if the changes in volume are strictly adiabatic  $DQ = 0$ , so

$$T_1 = \frac{\gamma - 1}{\gamma} \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1. \quad (13)$$

Let

$$\phi = T_1 - \frac{\gamma - 1}{\gamma} \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1. \quad (14)$$

Then  $\nabla^2 \phi = \nabla^2 T_1$  for  $\nabla^2 P_1 = 0$  and  $\left(\frac{\gamma-1}{\gamma} P_1 \nabla^2 \left(\frac{\partial T_0}{\partial P_0}\right)_{v_0}\right) \ll \nabla^2 T_1$ .

The error is not greater than 0.04%. Accordingly Equation (12) reduces to

$$\nabla^2 \phi = i\alpha^2 \phi, \quad (15)$$

where

$$\alpha^2 = \frac{\omega C_p \rho}{k}. \quad (16)$$

For the solution of Equation (15) it is to be noted that if the changes of volume are strictly isothermal  $T = T_0$  and  $T_1 = 0$ . If, on the other hand, they are strictly adiabatic

$$T_1 = \frac{\gamma-1}{\gamma} \left(\frac{\partial T_0}{\partial P_0}\right)_{v_0} P_1. \quad (16a)$$

At the wall of the chamber the changes in volume are nearly but not quite isothermal, since they partake a little of the adiabatic character. The temperature of the gas at the wall rises and falls slightly, as heat is conducted to and from the gas.

Accordingly the boundary condition may be written

$$T_1 = \xi \left(\frac{\gamma-1}{\gamma}\right) \left(\frac{\partial T_0}{\partial P_0}\right)_{v_0} P_1, \quad (17)$$

when  $\xi$  is a small fraction, for the moment completely undetermined. At the boundary then by Equation (14)

$$\phi = -(1-\xi) \left(\frac{\gamma-1}{\gamma}\right) \left(\frac{\partial T_0}{\partial P_0}\right)_{v_0} P_1. \quad (18)$$

At any point in the gas volume,  $\phi$  (real) is the difference between the actual temperature change and that which would be present if the gas behaved adiabatically (see Equation (16a)). It is important to notice this physical character.

### Spherical Gas Volume

Though the gas chambers used in these experiments are actually cylindrical, it was assumed in the early papers that they were spherical. The solution for the cylindrical cavity had not been found. The boundary conditions for the cylindrical case are naturally much less simple. Further, the solution for the spherical chamber was approximate only and not entirely satisfactory. The following solution for the spherical chamber is much better from every point of view. It will be followed by the solution for the cylindrical chamber.

For the spherically symmetrical chamber, we place  $\phi = \frac{U}{r}$ , and Equation (15) reduces to

$$\frac{d^2 U}{dr^2} = i\alpha^2 U. \quad (19)$$

Now  $\phi$  (real) must always be finite since it is a measure of temperature; then for  $r = 0$ ,  $\phi \neq \infty$ , so  $U = 0$ . Accordingly a solution of Equation (19) satisfying this condition is

$$\phi = \frac{A}{r} (e^{i^{1/2}\alpha r} - e^{-i^{1/2}\alpha r}). \quad (20)$$

At the boundary  $r = b$  we have from Equations (18) and (20)

$$A = -(1 - \xi) \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1 \frac{b}{e^{i^{\frac{1}{2}} \alpha b} - e^{-i^{\frac{1}{2}} \alpha b}}. \quad (21)$$

The mean value of  $\phi$  throughout the spherical volume is

$$\bar{\phi} = \frac{3}{4\pi b^3} \int_0^b \phi 4\pi r^2 dr = -\frac{3}{b^2} (1 - \xi) \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} \left\{ \frac{b}{i^{\frac{1}{2}}} \left( \frac{e^{i^{\frac{1}{2}} \alpha b} + e^{-i^{\frac{1}{2}} \alpha b}}{e^{i^{\frac{1}{2}} \alpha b} - e^{-i^{\frac{1}{2}} \alpha b}} \right) - \frac{1}{i\alpha^2} \right\} P_1. \quad (22)$$

In the experimental work to which these equations are to be applied  $\alpha \geq 20$  and  $b \approx 2$ . Therefore  $e^{-i^{\frac{1}{2}} \alpha b} \ll e^{i^{\frac{1}{2}} \alpha b}$ . So neglecting terms of 2nd order of magnitude and remembering that  $i^{-\frac{1}{2}} = \frac{1-i}{\sqrt{2}}$ , Equation (22) becomes

$$\bar{\phi} = -(1 - \xi) \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} \frac{3}{b} \left( \frac{1-i}{\alpha \sqrt{2}} \right) P_1. \quad (23)$$

So with Equation (14)

$$\bar{T}_1 = \left( \frac{\gamma - 1}{\gamma} \right) \left( 1 - \frac{3(1 - \xi)(1 - i)}{\alpha b \sqrt{2}} \right) \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1. \quad (24)$$

Combining Equations (9) and (24) with (7) and solving for  $P_1$  we get

$$P_1 = \frac{ax_1 \gamma \frac{v_0}{V_0} \left( \frac{\partial P_0}{\partial v_0} \right)_{T_0}}{1 + \frac{3}{b} \frac{(\gamma - 1)(1 - \xi)(1 - i)}{\alpha \sqrt{2}}}. \quad (25)$$

Put  $P_1 = M + iN$ ,  $\frac{3}{b} \frac{(\gamma - 1)(1 - \xi)}{\alpha \sqrt{2}} = G$ , and  $ax_1 \gamma \frac{v_0}{V_0} \left( \frac{\partial P_0}{\partial v_0} \right)_{T_0} = F$ .

Then equating real and imaginary quantities

$$\left. \begin{aligned} N &= \frac{G}{1+G} M & (a) \\ M &= \frac{F}{1+G+\frac{G^2}{1+G}} & (b) \end{aligned} \right\} \quad (26)$$

If  $G^2/1+G$  be replaced by  $G^2$ , the error introduced is less than 0.03%. Then

$$M = \frac{F}{1+G+G^2} = \frac{ax_1 \gamma \frac{v_0}{V_0} \left( \frac{\partial P_0}{\partial v_0} \right)_{T_0}}{1 + \frac{3}{b} \frac{(\gamma - 1)(1 - \xi)}{\alpha \sqrt{2}} + \left( \frac{3(\gamma - 1)(1 - \xi)}{\alpha b \sqrt{2}} \right)^2} \quad (27)$$

From the above and Equation (4b),  $P_{real} = P_0 + M \cos \omega t - N \sin \omega t$ .

The force acting per unit area of the piston, as given by Equation (8), is seen to be

$$\text{Real}(P_2 - P_1) = 2(P_{\text{real}} - P_0) = M \cos \omega t - N \sin \omega t. \quad (28)$$

The  $M$  component is seen from Equation (1) to be in phase with the displacement, and it acts like a restoring force, while the  $N$  component is  $90^\circ$  out of phase with the displacement, that is, in phase with the velocity, and acts as a dissipative force. It makes itself felt as an added friction or as a drag on the piston.

In Part I of this series of papers it is shown that the equation of motion for the oscillation of the piston leads to the following equation connecting the frequency at maximum amplitude with the restoring force acting on the piston ( $M$  in Equation (28)),

$$\omega_m^2 = \frac{2aM}{x_1(m + m_0)} - \frac{\beta'^2}{2}. \quad (29)$$

The squared term on the right-hand side arises from the fact that the maximum amplitude is displaced from the resonance frequency by a term involving the friction  $\beta'$ .  $M$  replaces the quantity  $\Delta P$  of the earlier papers,  $\omega_m = 2\pi f_m$  (where  $f_m$  is the frequency at maximum amplitude),  $a$  is the piston area,  $m + m_0$  is the effective mass of the oscillating system, and  $\beta'$  is the friction proper increased by the effect of the non-adiabatic behaviour of the gas (the part  $N$  of Equation (28)).

Substituting the value of  $M$  from Equation (27) into Equation (3) and solving for  $\gamma$ ,

$$\gamma = -\left(\omega_m^2 + \frac{\beta'^2}{2}\right) \frac{(m + m_0)V_0 P_0}{2a^2 P_0} \frac{(\partial v_0)}{v_0} \left(\frac{\partial P_0}{\partial P_0}\right)_{T_0} \left[1 + \frac{3}{b}(\gamma - 1)(1 - \xi) \left(\frac{k}{2\rho C_p \omega}\right)^{\frac{1}{2}} + \left(\frac{3}{b}(\gamma - 1)(1 - \xi) \left(\frac{k}{2\rho C_p \omega}\right)^{\frac{1}{2}}\right)^2\right]. \quad (30)$$

If the volume changes were strictly adiabatic

$$\gamma' = -\left(\omega_m^2 + \frac{\beta'^2}{2}\right) \frac{(m + m_0)V_0 P_0}{2a^2 P_0} \frac{(\partial v_0)}{v_0} \left(\frac{\partial P_0}{\partial P_0}\right)_{T_0}, \quad (31)$$

so that the effect of the non-adiabatic change may be written as a correction factor

$$\gamma = \Gamma \gamma', \quad (32)$$

where

$$\Gamma = 1 + \frac{3}{b}(\gamma - 1)(1 - \xi) \left(\frac{k}{2\rho C_p \omega}\right)^{\frac{1}{2}} + \left(\frac{3}{b}(\gamma - 1)(1 - \xi) \left(\frac{k}{2\rho C_p \omega}\right)^{\frac{1}{2}}\right)^2. \quad (33)$$

In the earlier paper the correction applied was in the form of an additive quantity written

$$\gamma_{\text{corr.}} = \gamma' + \Delta\gamma,$$

where

$$\Delta\gamma = \frac{3}{b}(\gamma - 1) \left(\frac{k}{2\rho C_p \omega}\right)^{\frac{1}{2}}. \quad (34)$$

*Note:—We distinguish between corrected values as previously obtained and written  $\gamma_{\text{corr.}}$  and the corrected values using the new factor deduced in this paper and written simply  $\gamma$  (see Equation (30)).*



Since values of  $\Delta\gamma$  have already been published, it will be useful to express  $\Gamma$  in terms of  $\Delta\gamma$ . Equations (33) and (34) give this relation

$$\Gamma = 1 + (1 - \xi) \frac{\Delta\gamma}{\gamma} + (1 - \xi)^2 \left( \frac{\Delta\gamma}{\gamma} \right)^2. \quad (35)$$

The value  $\gamma'$  is found as though the gas behaved adiabatically, and it is used as an approximate value to give the corrected value. This corrected value may be applied to give a second approximation. The first approximation was found to be sufficient to give the accuracy sought.

### Cylindrical Volume of Finite Length

The gas chambers in the apparatus are cylindrical instead of spherical. The following analysis shows that the correction factor is the same for either case, to a good order of approximation.

The cylinder is assumed to have length  $2c$  and radius  $d$ . The equation for heat flow is as before

$$\nabla^2 \phi = i\alpha^2 \phi.$$

A solution of the form

$$\phi = R(x) X(x) \quad (36)$$

may be found.

Accordingly, in cylindrical co-ordinates

$$\frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} + m^2 R = 0, \quad (37)$$

and

$$\frac{d^2 X}{dx^2} - (i\alpha^2 + m^2) X = 0, \quad (38)$$

where  $m^2$  is the constant of separation. The general solution of these equations, with the origin at the centre of the cylinder so chosen that  $\phi(x) = \phi(-x)$ , is

$$\phi = \sum_0^{\infty} A_n J_0(m_n r) \cosh(p_n x), \quad (39)$$

where

$$p_n^2 = m^2 + i\alpha^2. \quad (40)$$

To solve for the constants of Equation (39) in terms of the boundary conditions it will be convenient to assume

$$\phi = \phi_x + \phi_r, \quad (41)$$

where

$$\phi_x = 0 \text{ at } r = d,$$

$$\phi_x = -(1 - \xi) \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1, \text{ at } x = \pm c, \quad (42)$$

and

$$\phi_r = 0 \text{ at } x = \pm c,$$

$$\phi_r = -(1 - \xi) \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1 \text{ at } r = d. \quad (43)$$



These conditions imposed on  $\phi$  are in agreement with Equation (18) except at the ends at the periphery where at  $r = d$  and  $x = \pm c$  Equations (42) and (43) are inconsistent. The discontinuity in the surface at the ends introduced complications in the solution, but the boundary conditions as given are quite satisfactory. There seems to be some physical significance to writing  $\phi$  in the form of Equation (41). It will be recalled that  $\phi$  is a quantity that measures the departure of the behaviour of the gas from the true adiabatic, so the effect of the boundary on  $\phi$  is taken as the sum of the effects at the plane and curved walls respectively.

Making Equation (39) satisfy the conditions of Equation (42) gives

$$\phi_x = -(1 - \xi) \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1 \sum_{s=0}^{\infty} \frac{2}{\lambda_s} \frac{J_0 \left( \lambda_s \frac{r}{d} \right) \cosh(p_s x)}{J_1(\lambda_s) \cosh(p_s c)}, \quad (44)$$

and making Equation (39) satisfy Equation (43) gives

$$\phi_r = -(1 - \xi) \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1 \sum_{s=0}^{\infty} (-1)^s \frac{4}{(2s + 1)\pi} \frac{J_0(m_s r)}{J_0(m_s d)} \times \cos \left( (s + \frac{1}{2}) \pi \frac{x}{c} \right), \quad (45)$$

where  $J_0(\lambda_s) = 0$  or  $\lambda_s$  is the  $s^{\text{th}}$  root of the zero order Bessel function

$$p_s^2 = \left( \frac{\lambda_s}{d} \right)^2 + i\alpha^2, \quad m_s^2 = - \left\{ \left( (s + \frac{1}{2}) \frac{\pi}{c} \right)^2 + i\alpha^2 \right\} \quad (46)$$

Therefore the average value of  $\phi$  over the volume is

$$\bar{\phi} = \frac{1}{V_0} \int_0^d 2\pi r dr \int_{-c}^c \phi dx = -(1 - \xi) \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} P_1 \times \left\{ \sum_{s=0}^{\infty} \left( \frac{2}{\lambda_s} \right)^2 \frac{\tanh p_s c}{p_s c} + \left( \frac{2}{\pi} \right)^2 \sum_{s=0}^{\infty} \frac{1}{m_s d} \left( \frac{2}{2s + 1} \right)^2 \frac{J_1(m_s d)}{J_0(m_s d)} \right\} \quad (47)$$

For the values of  $\alpha$ ,  $c$ , and  $d$  used in the experimental work to which Equation (47) was applied ( $\alpha \geq 20$ ,  $c \approx 10$ ,  $d \approx 2$ ), the two series may be summed approximately, giving

$$\bar{\phi} = -(1 - \xi) \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\partial T_0}{\partial P_0} \right)_{v_0} \left( \frac{1}{c} + \frac{2}{d} \right) \frac{(1 - i)}{\alpha \sqrt{2}} P_1, \quad (48)$$

where we have taken

$$\sum_{s=0}^{\infty} \frac{1}{\lambda_s^2} = \frac{1}{4} \quad \text{and} \quad \left( \frac{2}{\pi} \right)^2 \sum_{s=0}^{\infty} \frac{1}{(2s + 1)^2} = \frac{1}{2}.$$

For the cylinder the ratio of wall area to volume is  $\left( \frac{1}{c} + \frac{2}{d} \right)$ , while for the sphere it is  $\frac{3}{d}$ .

Therefore Equations (48) and (23) are identical when expressed in terms of wall area and volume.

Calculation may be made therefore as though the cavities were spherical.

### Calculations

The new values of  $\gamma$  may be obtained from the published values of  $\gamma_{corr.}$ ,  $\Delta\gamma$ , and  $\Gamma$ , where  $\gamma_{corr.}$  represents the value obtained by the less rigid method of the earlier papers,  $\Delta\gamma$  is the additive correction for non-adiabatic behaviour, and  $\Gamma$  is the new correction factor (see Equation (33)).

It will be remembered that for the noble gases (approximately ideal) the curve showing the relation between pressure and the ratio  $\gamma$  is a straight line. The diagrams of the early papers show this clearly. This is also shown to be necessary by the theoretical discussions of Appendix IV of the second article. Also, it will be noted that the correction to be applied to the experimental results to compensate for the departure from true adiabatic behaviour of the gas is large for low pressures and very small for high pressures. The error in computing the correction is negligible at the high pressures although probably considerable at low pressures since it varies inversely as the square root of the frequency.

We may then extrapolate the corrected high pressure results as a straight line into the low pressure region and calculate the value of  $\xi$  necessary to make the low pressure values of  $\gamma$  fall on this extrapolated line. Calculations on the data obtained with different gases show that  $\xi$  varies but little from gas to gas, so that it may be taken as constant. The value finally adopted is  $\xi = 0.13$ , which means that the discontinuity in temperature at the gas-metal surface is 13% of what would obtain if no heat exchange took place between the gas and the walls.

The following tables give the recalculated values of  $\gamma$ . It will be seen that only a few points at low pressure are affected and then only little, except in the case of helium for which gas there is still something to be desired.

Equations fitted by the method of least squares are given above each table, and values of  $\gamma_{calc.}$  from these equations are listed in column six and compared in column seven to the experimental values. In Tables IVa and Va, the measurements on helium and hydrogen are extended to 60 atm. pressure. In carrying out these measurements a new and heavier piston was used to keep the frequency down below 150 cycles per sec. (the limit of the frequency measuring apparatus). The weight of the new piston was  $603.65 \pm 0.01$  gm. and the resulting gas volume was  $74.42 \pm 0.01$  cc. The other constants of the apparatus remain as already published (1, 2). This gives

$$\gamma = 0.42159 \frac{f_m^2}{h} \Delta\chi G \Gamma = \gamma' \Gamma, \quad (49)$$

with  $f_m$  measured in cycles per second and  $h$  in centimetres of mercury at  $0^\circ$  C. and where the factors are

$$\Lambda = 1 + \frac{m_g}{m}, \quad (a)$$

$$G = - \frac{P_0}{v_0} \left( \frac{\partial v_0}{\partial P_0} \right)_{T_s}, \quad (b) \quad (50)$$

$$\chi = 1 + \frac{1}{2} \left( \frac{\beta'}{\omega} \right)^2. \quad (c)$$

For the calculation of  $\Gamma$  the ratio  $\frac{\text{wall area}}{\text{volume}}$  for this apparatus is 1.338.

It was found that the factor  $\chi$  was in all cases never far from unity (actually 1.00001 or better), and it was therefore neglected. To calculate  $\Lambda$  and  $G$ , recourse was had to published experimental  $Pv$  data. For helium the  $Pv$  data of Keesom and Van Santen (9) as given in Part II were used, but for hydrogen

TABLE I  
ARGON AT 24.2° C.

$$\gamma_{\text{calc.}} = 1.6667 + 0.00353P$$

$P$	$\gamma'$	$\Delta\gamma$	$\Gamma$	$\gamma$	$\gamma_{\text{calc.}}$	$(\gamma - \gamma_{\text{calc.}})10^3$
0.9886	1.6403	0.0252	1.0172	1.668 <sub>s</sub>	1.6702	-2
2.256	1.6594	0.0136	1.0092	1.675	1.6747	0
4.783	1.6751	0.0079	1.0053	1.684	1.6836	0
6.722	1.6838	0.0062	1.0042	1.691	1.6904	+1
8.741	1.6919	0.0051	1.0034	1.698	1.6976	0
10.719	1.7006	0.0044	1.0029	1.705 <sub>s</sub>	1.7043	+1
12.698	1.7071	0.0039	1.0026	1.711 <sub>s</sub>	1.7115	0
14.704	1.7139	0.0036	1.0023	1.717	1.7186	-2
16.670	1.7212	0.0033	1.0021	1.725	1.7255	0
18.658	1.7290	0.0030	1.0020	1.732 <sub>s</sub>	1.7326	0
20.688	1.7372	0.0028	1.0018	1.740	1.7397	0

$$\Lambda = 1 + \frac{m_g}{m},$$

$$G = -\frac{P_0}{v_0} \left( \frac{\partial v_0}{\partial P_0} \right)_{T_0},$$

$\Gamma$  = Correction factor for non-adiabatic behaviour,

$\gamma'$  value obtained as though gas behaved adiabatically,

$\Delta\gamma$ , old additive corrective term,

$\gamma$ , corrected value,

$\gamma_{\text{calc.}}$  value obtained from equation fitted by least squares.

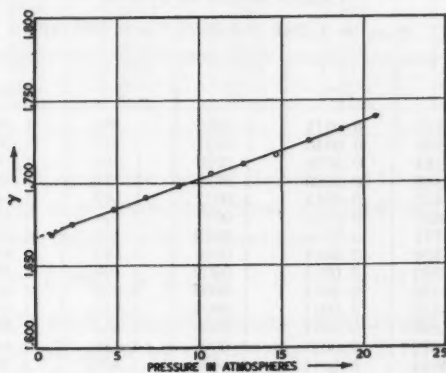


FIG. 2. Argon at 24.2° C.  $\gamma$  as a function of pressure.

TABLE II  
NITROGEN AT 23° C.

$$\gamma_{\text{calc.}} = 1.4006 + 0.00221P$$

$P$	$\gamma'$	$\Delta\gamma$	$\Gamma$	$\gamma$	$\gamma_{\text{calc.}}$	$(\gamma - \gamma_{\text{calc.}})10^3$
0.9984	1.3876	0.0148	1.0110	1.402 <sub>s</sub>	1.4028	-0
3.668	1.4024	0.0056	1.0042	1.408	1.4087	-1
5.389	1.4083	0.0042	1.0032	1.413	1.4125	0
6.751	1.4124	0.0036	1.0027	1.416	1.4155	0
8.056	1.4143	0.0032	1.0023	1.417 <sub>s</sub>	1.4184	+1
10.516	1.4213	0.0027	1.0019	1.424	1.4239	0
13.032	1.4287	0.0023	1.0016	1.431	1.4294	+2
15.659	1.4314	0.0021	1.0015	1.433 <sub>s</sub>	1.4352	-2
21.219	1.4445	0.0017	1.0012	1.446 <sub>s</sub>	1.4473	-1
25.929	1.4565	0.0015	1.0011	1.458	1.4580	0

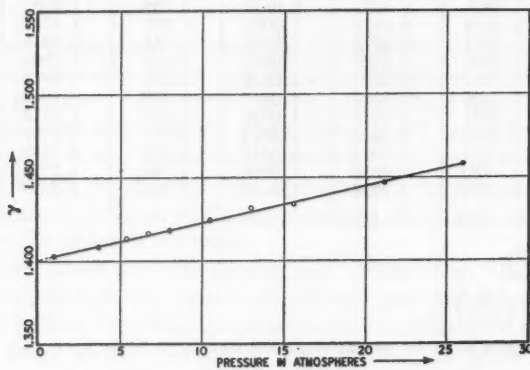


FIG. 3. Nitrogen at 23.0° C.  $\gamma$  as a function of pressure.

TABLE III  
CARBON DIOXIDE AT 23.8° C.

$$\gamma_{\text{calc.}} = 1.2948 + 0.00500P + 0.000179P^2$$

$P$	$\gamma'$	$\Delta\gamma$	$\Gamma$	$\gamma$	$\gamma_{\text{calc.}}$	$(\gamma - \gamma_{\text{calc.}})10^3$
0.9917	1.2922	0.0074	1.0057	1.299 <sub>s</sub>	1.3000	-0.5
2.273	1.3035	0.0040	1.0031	1.307 <sub>s</sub>	1.3071	0
4.240	1.3164	0.0026	1.0020	1.319	1.3192	0
6.119	1.3315	0.0020	1.0015	1.333 <sub>s</sub>	1.3321	+1
8.130	1.3473	0.0017	1.0012	1.349	1.3472	+2
10.103	1.3625	0.0015	1.0011	1.364	1.3636	0
12.054	1.3791	0.0014	1.0010	1.380 <sub>s</sub>	1.3811	-1
12.101	1.3806	0.0014	1.0010	1.382	1.3816	0
13.991	1.3982	0.0013	1.0009	1.399 <sub>s</sub>	1.3998	0
16.121	1.4188	0.0012	1.0009	1.420	1.4219	-2
18.071	1.4424	0.0011	1.0008	1.443 <sub>s</sub>	1.4436	0
20.036	1.4649	0.0011	1.0008	1.466	1.4668	-1
21.840	1.4879	0.0011	1.0008	1.489	1.4893	0
22.223	1.4944	0.0011	1.0008	1.495 <sub>s</sub>	1.4943	+1

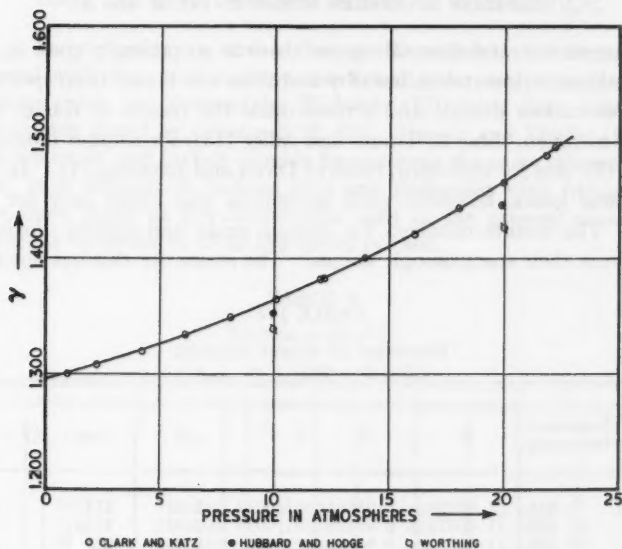
FIG. 2. Carbon dioxide at 23.8° C.  $\gamma$  as a function of pressure.

TABLE IV

HYDROGEN AT 24.4° C.

$$\gamma_{\text{calc.}} = 1.4045 + 0.00025P$$

$P$	$\gamma'$	$\Delta\gamma$	$\Gamma$	$\gamma$	$\gamma_{\text{calc.}}$	$(\gamma - \gamma_{\text{calc.}})10^3$
0.9874	1.3617	0.0394	1.0298	1.4023	1.4047	-2.4
2.283	1.3835	0.0210	1.0156	1.405	1.4051	0
4.161	1.3902	0.0133	1.0099	1.404	1.4055	-1
6.994	1.3970	0.0090	1.0066	1.406	1.4052	0
10.088	1.3996	0.0069	1.0051	1.407	1.4070	0
12.988	1.4019	0.0056	1.0040	1.407 <sub>6</sub>	1.4077	0
15.964	1.4051	0.0049	1.0035	1.410	1.4085	+1
19.034	1.4067	0.0043	1.0031	1.411	1.4092	+2
22.165	1.4057	0.0038	1.0027	1.409 <sub>6</sub>	1.4100	0
24.961	1.4070	0.0035	1.0025	1.410 <sub>6</sub>	1.4107	0

it was felt advisable to use the data of Holborn and Otto (7), which are valid over a wider range of pressures than those of Nijhoff and Keesom (11) (used in Part II). These data give by interpolation

$$(Pv)_{24.4^\circ} = 1.08865 + 0.6496 \times 10^{-3} P + 0.115 \times 10^{-6} P^2.$$

As before, Amagat units of specific volume for hydrogen were converted to cubic centimetres per gram by multiplying  $v$  by 11127.4; for helium, by 5603.33.

For monatomic and diatomic gases there is surprisingly good agreement between the experimental values of  $\gamma$  and those calculated from spectroscopic data. For carbon dioxide and nitrous oxide the results of Kassel (8) were used; for nitrogen, those of Trautz and Adler (13); for sulphur dioxide, those of Cross (3); and for hydrogen, those of Davis and Johnston (4). In the case of triatomic gases, however, good agreement was found only for sulphur dioxide. The results obtained for nitrous oxide and carbon dioxide differ greatly from their spectroscopic values. The reason for this has not yet been

TABLE IVa  
HYDROGEN AT HIGHER PRESSURE

$P$	Resonance frequency	$\Lambda$	$G$	$\Gamma$	$\gamma$	$\gamma_{calc.}$	$(\gamma - \gamma_{calc.})10^3$
22.512	76.034	1.00024	0.98663	1.0039	1.411	1.4101	+1
26.619	82.820	1.00027	0.98422	1.0035	1.412	1.4111	+1
30.704	89.106	1.00031	0.98182	1.0031	1.413	1.4122	+1
34.608	94.747	1.00035	0.97952	1.0029	1.414	1.4131	+1
38.536	100.042	1.00038	0.97722	1.0027	1.412	1.4141	-2
42.718	105.569	1.00042	0.97495	1.0025	1.415	1.4152	0
46.587	110.395	1.00046	0.97199	1.0023	1.414	1.4162	-2
50.784	115.480	1.00050	0.97008	1.0022	1.417	1.4172	0
54.534	119.938	1.00054	0.96788	1.0021	1.420	1.4181	+2
58.874	124.893	1.00058	0.96555	1.0020	1.419	1.4192	0

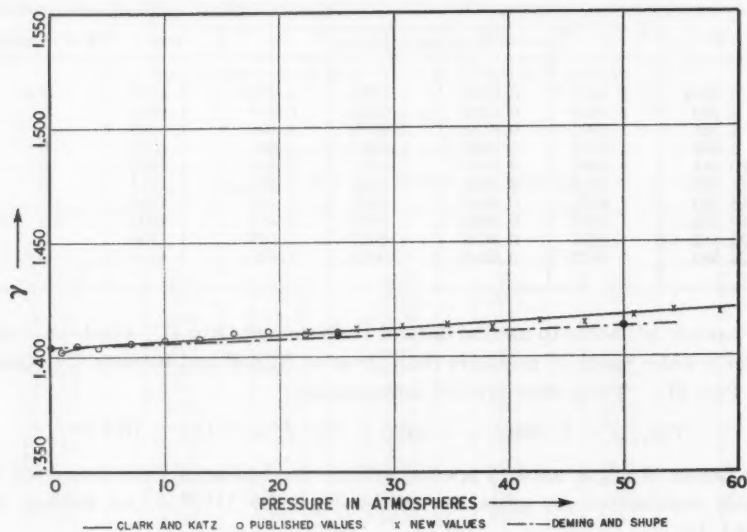


FIG. 5. Hydrogen at 24.4° C.  $\gamma$  as a function of pressure.

given. It is interesting to notice that no dispersion\* with frequency has been found with any of the above-mentioned gases except carbon dioxide and nitrous oxide, as observed by Richards (12) (very little dispersion in sulphur dioxide found by Grossman (5, 6)). Kneser and Zühlke (10) found that nitrous oxide and carbon dioxide have almost the same relaxation time. However, it is difficult to believe that any dispersion with frequency can exist for these gases at low frequencies used in the present experiment—frequencies of the order of 25 to 150 cycles per sec.

TABLE V

HELIUM AT 23.1° C.

$$\gamma_{\text{calc.}} = 1.6669 - 0.0002P$$

P	$\gamma'$	$\Delta\gamma$	$\Gamma$	$\gamma$	$\gamma_{\text{calc.}}$	$(\gamma - \gamma_{\text{calc.}})10^3$
0.9951	1.5732	0.0745	1.0528	1.6563	1.6667	-10.4
2.275	1.6127	0.0398	1.0280	1.658	1.6664	-8
5.283	1.6380	0.0210	1.0144	1.662	1.6657	-4
7.871	1.6444	0.0156	1.0106	1.662	1.6652	-3
9.861	1.6489	0.0131	1.0090	1.664	1.6647	-1
11.754	1.6510	0.0115	1.0078	1.664	1.6642	0
13.800	1.6523	0.0102	1.0069	1.664	1.6639	0
15.929	1.6524	0.0091	1.0061	1.662	1.6634	0
17.623	1.6531	0.0084	1.0057	1.6625	1.6630	0
19.943	1.6522	0.0078	1.0053	1.661	1.6625	-1

TABLE Va

HELIUM AT HIGHER PRESSURE

P	Resonance frequency	$\Lambda$	G	$\Gamma$	$\gamma$	$\gamma_{\text{calc.}}$	$(\gamma - \gamma_{\text{calc.}})10^3$
14.020	64.770	1.00028	0.99367	1.0097	1.666	1.6638	+2
18.588	74.661	1.00037	0.99166	1.0078	1.663	1.6628	0
22.590	82.388	1.00045	0.98992	1.0068	1.662	1.6619	0
26.689	89.723	1.00054	0.98816	1.0059	1.661	1.6610	0
30.471	95.813	1.00061	0.98655	1.0054	1.659	1.6602	-1
34.194	101.690	1.00068	0.98498	1.0033	1.654	1.6540	0
38.482	107.896	1.00077	0.98319	1.0049	1.662	1.6594	+3
42.539	113.444	1.00085	0.98152	1.0045	1.659	1.6584	+1
46.774	119.151	1.00093	0.97979	1.0042	1.656	1.6575	-1
50.818	124.156	1.00101	0.97815	1.0039	1.658	1.6566	+1
54.464	128.772	1.00108	0.97669	1.0036	1.653	1.6557	-2
58.487	133.417	1.00116	0.97510	1.0034	1.657	1.6549	+2

\* When kinetic energy is given to a group of molecules the time required for this energy to be distributed among the vibrational degrees of freedom is known as the relaxation time. Dispersion of sound with frequency is the phenomenon which occurs when the frequency is so great as to be comparable to the relaxation time. This phenomenon appears as a change of velocity of sound, change of the ratio of the specific heats of the gas, and of some related quantities.



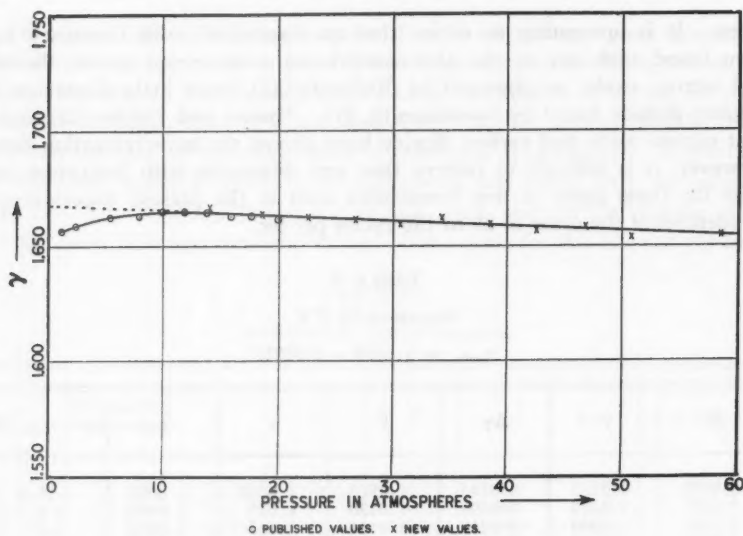
FIG. 6. Helium at 23.1° C.  $\gamma$  as a function of pressure.

Table VI gives a summary of results together with results obtained by spectroscopic methods by various observers.

TABLE VI

Gas	Temp., °C.	Present work		Spectroscopic methods 0 atm.	Diff., %
		1 Atm.	0 Atm.		
Monatomic	A 24.2	1.670 <sub>2</sub>	1.666 <sub>7</sub>	1.6667	0.00
	He 23.0	1.666 <sub>7</sub>	1.666 <sub>9</sub>	1.6667	-0.01
Diatomic	N <sub>2</sub> 23.0	1.402 <sub>3</sub>	1.400 <sub>6</sub>	1.3999	+0.05
	H <sub>2</sub> 24.4	1.404 <sub>7</sub>	1.404 <sub>6</sub>	1.4050	-0.04
Triatomic	SO <sub>2</sub> 25.1	1.283 <sub>7</sub>	1.264 <sub>2</sub>	1.2642	0.00
	N <sub>2</sub> O 25.1	1.284 <sub>7</sub>	1.278 <sub>3</sub>	1.2735	+0.38
	CO <sub>2</sub> 23.8	1.300 <sub>0</sub>	1.294 <sub>8</sub>	1.2885	+0.49

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NUMBER 1

## THE SYNTHESIS OF 2-KETOCYCLOHEXYLSUCCINIC ACID AND RELATED SUBSTANCES

### I. SYNTHESSES INVOLVING CYCLOHEXENE OXIDE<sup>1</sup>

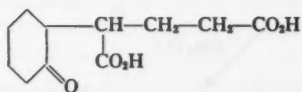
By JOHN A. McRAE<sup>2</sup>, E. HAROLD CHARLESWORTH<sup>3</sup>, AND D. S. ALEXANDER<sup>4</sup>

#### Abstract

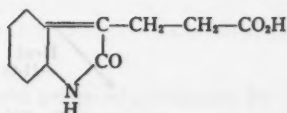
A synthesis of 2-ketocyclohexylsuccinic acid is described. This substance has been prepared by the oxidation of the  $\gamma$ -lactone of cyclohexanolsuccinic acid, which results from the condensation of cyclohexene oxide, the sodio-derivative of malonic ester, and ethyl bromoacetate, followed by hydrolysis and decarboxylation. The lactone of the keto acid and the lactam formed when the keto acid is treated with alcoholic ammonia are described. 2-Ketocyclohexylacetic and 2-ketocyclohexylmalonic acids have also been prepared. Alkyl halides may be substituted for ethyl bromoacetate in the above reaction. Methyl iodide yields the  $\gamma$ -lactone of cyclohexanol- $\alpha$ -propionic acid and benzyl chloride the  $\gamma$ -lactone of cyclohexanol- $\alpha$ -benzylacetic acid. Oxidation of these lactones with bromine and magnesium hydroxide yields 2-ketocyclohexyl- $\alpha$ -propionic acid and 2-ketocyclohexylbenzylacetic acid.

#### Introduction

A synthesis of  $\alpha$ -(2-ketocyclohexyl) glutaric acid (I), its anhydro derivative, and its lactam (II) was accomplished by Kendall, Osterberg, and MacKenzie (8, 9).



I



II

An extension of this method of synthesis to other ketocyclohexyl acids, with a study of the stability of their lactams, seemed desirable. The general method involved is given below for the preparation of 2-ketocyclohexylsuccinic acid. Cyclohexene oxide (III) was condensed with the sodio-derivative of malonic ester and ethyl bromoacetate; this yielded the tricarboxylic ester (IV). Hydrolysis of this ester followed by decarboxylation produced the lactone of cyclohexanolsuccinic acid (V). When this lactone was oxidized either by bromine in the presence of magnesium hydroxide or by alkaline permanganate

<sup>1</sup> Manuscript received October 18, 1942.

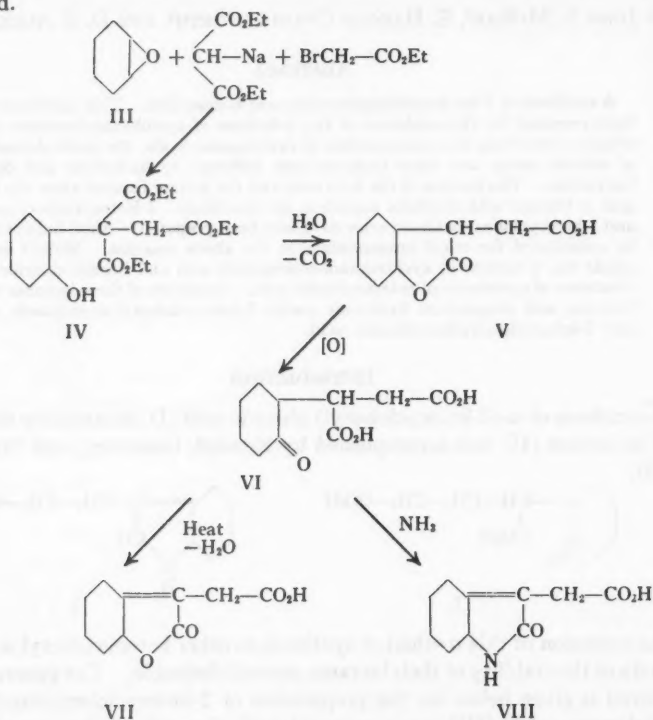
Contribution from the Departments of Chemistry, University of Manitoba, Winnipeg, Man., and Queen's University, Kingston, Ont.

<sup>2</sup> Professor of Chemistry, Queen's University.

<sup>3</sup> Lecturer in Chemistry, University of Manitoba.

<sup>4</sup> Holder of a Bursary under the National Research Council of Canada, 1939-1940.

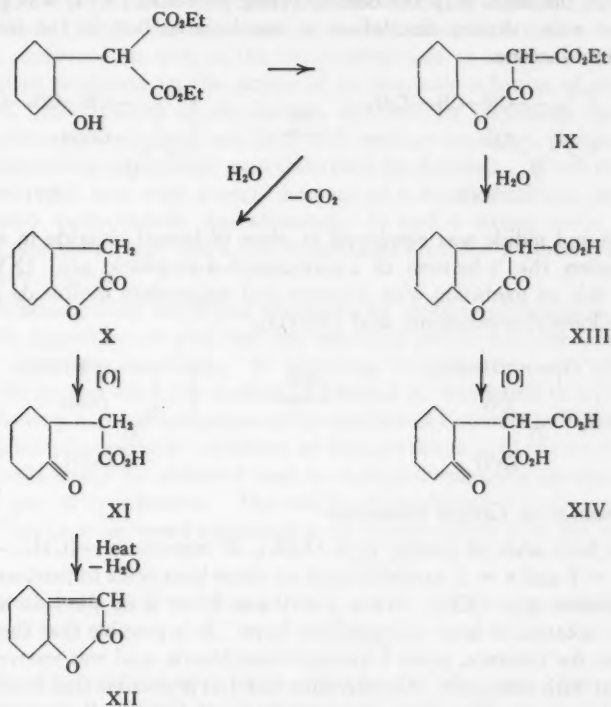
2-ketocyclohexylsuccinic acid (VI) resulted. On heating *in vacuo* at 200° C., a molecule of water was lost and the unsaturated lactone (VII)\* produced. When the keto acid (VI) was treated with alcoholic ammonia under pressure the lactam (VIII)\* was produced. This lactam was reasonably stable to water, but was decomposed by cold 1.25 *N* sodium hydroxide solution, whereas Kendall and his associates (9) found the corresponding glutaric derivative (II) stable at this alkalinity even up to 80°, although it was decomposed by boiling concentrated alkaline solutions, with regeneration of the keto acid.



Coffey (4) prepared the ester lactone (IX) by condensation of cyclohexene oxide with the sodio-derivative of malonic ester, and, on hydrolysis and decarboxylation, cyclohexanolacetic lactone (X). By oxidation with bromine and magnesium hydroxide 2-ketocyclohexylacetic acid (XI) has now been obtained. By dehydration of (XI) the anhydro derivative, which must have the unsaturated lactonic structure (XII), was produced. It was likely that a

\* The 3-3a position of the double bond in the lactone and lactams is based on the work of Kendall and Osterberg (8), who proved that in the case of the corresponding glutaric derivatives the bond occupied this position.

lactam of (XI) was produced by treatment with alcoholic ammonia, but it was so unstable that it decomposed during attempts at purification.

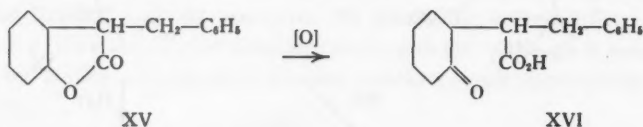


2-Ketocyclohexylacetic acid (XI) has been prepared previously by Chuang and Ma (3), Chatterjee (2), and Ghosh (7). In none of these preparations was the product seemingly as pure as the sample prepared in the present work, which has a melting point of more than 30° higher than that of the Chinese authors.

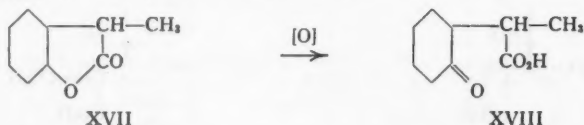
If the ester lactone (IX), after hydrolysis, was not subjected to decarboxylation but oxidized directly either by bromine and magnesium hydroxide or by alkaline permanganate, 2-ketocyclohexylmalonic acid (XIV) resulted. This acid was rather unstable, tending to decompose with loss of carbon dioxide at its melting point. Attempts to produce a lactam were unsuccessful, decarboxylation occurring under these conditions, and the nitrogenous compound isolated, which was probably identical with that obtained from 2-ketocyclohexylacetic acid, was very unstable.

When cyclohexene oxide, the sodio-derivative of malonic ester, and benzyl chloride were condensed, hydrolysed and decarboxylated, the lactone of cyclohexanolbenzylacetic acid (XV) was isolated. Contrasting with the condensations with  $\beta$ -bromopropionic ester and bromoacetic ester, where the con-

densation occurs at room temperature, many hours refluxing are necessary for condensation in the case of benzyl chloride and alkyl halides. When (XV) is oxidized in the usual way the corresponding keto-acid (XVI) was produced. As it lost water during distillation, it was isolated best in the form of its unsaturated lactone.

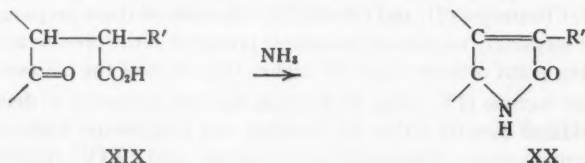


When methyl iodide was employed in place of benzyl chloride in the latter condensation the  $\gamma$ -lactone of cyclohexanol- $\alpha$ -propionic acid (XVII) was formed; this on oxidation with bromine and magnesium hydroxide produced 2-ketocyclohexyl- $\alpha$ -propionic acid (XVIII).



#### Some Remarks on Lactam Formation

In the keto acids of general type (XIX),  $\text{R}'$  represents  $-(\text{CH}_2)_x-\text{COOH}$ . When  $x = 1$  and  $x = 2$ , ammonia acts on these keto acids to produce lactams of the general type (XX). When  $x = 0$  and  $\text{R}' = \text{H}$  or alkyl, lactams have not been isolated, at least in crystalline form. It is possible that they are not produced; for instance, some 2-ketocyclohexylacetic acid was recovered after treatment with ammonia. On the other hand, it is possible that these lactams have a transitory existence and are hydrolysed by the alkaline medium in which they are produced or during isolation and purification.



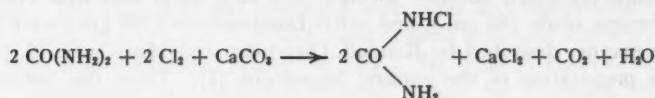
There is some evidence to support the latter view, as lactams in which  $\text{R}'$  is present are known to hydrolyse in alkaline media. It has been noticed also that the lactam in which  $x = 1$  is less stable than when  $x = 2$ . When  $x = 0$  the lactam has not been isolated. Presumably if  $x > 2$ , the lactams would be still more stable than when  $x = 2$ .

The oil produced from the alcoholic ammonia treatment of 2-ketocyclohexylbenzylacetic acid loses ammonia on warming. Further work is proceeding in connection with the hydrolysis of lactams where  $\text{R}' = \text{alkyl}$ .

### Experimental

The synthesis of  $\alpha$ -(2-ketocyclohexyl) glutaric acid by Kendall, Osterberg, and MacKenzie (9) has been repeated and the lactone structure of its anhydro-derivative confirmed, as well as the hexahydroindole or lactam structure of the derivative produced by the action of an alcoholic solution of ammonia on the acid. Bromination of the lactam, followed by successive reduction first with zinc and acetic acid and then with sodium amalgam, produced the 2-ketodihydroindole-3-propionic acid described by Kendall. When this acid was distilled with zinc dust a small amount of a liquid distillate, probably identical with 3-ethylindole, was obtained. It had a strong faecal odour, gave a red pine splint test, and a red colour with Ehrlich's *p*-dimethylamino-benzaldehyde reagent.

The cyclohexene oxide employed was made by treating cyclohexene (Eastman's) with hypochlorous acid and the resulting *o*-chlorocyclohexanol with a solution of sodium hydroxide. In preparing the large amounts of hypochlorous acid for this work the method of Detœuf (6) was found to be exceedingly satisfactory and much superior to the method of Coleman and Johnstone (5). By Detœuf's method, solutions of hypochlorous acid 10 to 15% in strength could easily be obtained and in sufficient quantity to react with 300 to 400 gm. of cyclohexene. The weight of precipitated chalk employed by Detœuf has been increased somewhat to be in accordance with the reaction



The data for a typical run are given. Chlorine gas was passed into an ice-cooled mixture of urea (400 gm.), precipitated chalk (280 gm.), and water (275 cc.) for a period of 2.5 to 3 hr., by which time an increase in weight of 240 gm. had occurred. The mixture was then diluted with water to about 1400 cc. and the solid filtered off.

Volume of solution, 1355 cc., 14.6% in hypochlorous acid. 1 cc.  $\equiv$  55.8 cc. *N*/10 sodium thiosulphate  $\equiv$  0.228 gm. cyclohexene.

Ice (600 gm.), water (600 cc.), the monochlorourea solution (1350 cc.), and cyclohexene (340 gm., 10% in excess) were placed in a 5 litre flask and stirred mechanically, or in a gallon bottle and shaken by hand or by machine, until the top layer of cyclohexene had disappeared and a heavy white oil was on the bottom. This required about two hours, at the end of which time titration showed that there was no hypochlorous acid present. The *o*-chlorocyclohexanol (390 gm., 70% theoretical) was isolated by steam distillation and extraction with ether. It boiled at 95 to 105° (40 mm.).

#### Monobromourea Solution and *o*-Bromocyclohexanol

Detœuf's method has also been applied to the preparation of a hypobromous acid solution. The bromination was carried out in a three-necked 2 litre



flask equipped with dropping funnel, mechanical stirrer with mercury seal, and outlet tube. The flask was cooled in ice, and bromine (50 cc.) was added over a period of three hours to a mixture of urea (120 gm.), chalk (60 gm.), and water (60 cc.). At the end of the bromination, water (400 cc.) was added and the solution filtered. The solution obtained (550 cc.) contained 12.2% hypobromous acid. It was used with cyclohexene (62 gm.) in the production of *o*-bromocyclohexanol by the manner described above. A colourless oil (117 gm.), which was darkened by the action of light, and boiled at 98 to 105° (23 mm.) was obtained. These properties are in agreement with those described by Coffey (4) and Bedos (1).

#### *Cyclohexene Oxide (III)*

This was prepared from *o*-chlorocyclohexanol in 76% yield by the method of Osterberg (11). There was produced a fairly large amount, approximately one-third of the weight of the cyclohexene oxide, of residue boiling above 175° C. These residues boiling at 70 to 76° (10 mm.) or 188° (767 mm.) are thought to be 1 : 2-dichlorocyclohexane. Markownikoff (10) gives the boiling point of this compound as 187 to 189°.

Cyclohexene oxide has also been prepared from the sample of *o*-bromocyclohexanol described above.

#### *The Tri-ester (IV)*

Sodium (15 gm.), absolute alcohol (250 cc.), ethyl malonate (100 gm.), cyclohexene oxide (60 gm.), and ethyl bromoacetate (100 gm.) were treated in the manner described by Kendall, Osterberg, and MacKenzie (9, p. 1389) in the preparation of the glutaric homologue (I). From the benzene suspension the triester was obtained.

#### *Cyclohexanolsuccinic Lactone (V)*

This triester (80 gm.) was hydrolysed with 5 *N* sodium hydroxide solution (150 cc.), a little alcohol being added to clear the solution, which was refluxed on the sand-bath. When the saponification was complete the alcohol was removed by distillation up to 100° C. The solution was neutralized by an equivalent amount of 10 *N* sulphuric acid and boiled to close the lactone ring. The dicarboxylic lactone, which did not solidify, was extracted with ether. The oil remaining after removal of the ether was decarboxylated by heating to 220° in an oil-bath.

The crude cyclohexanolsuccinic lactone (V) (30 gm.) was purified by dissolving in hot benzene (charcoal). On the addition of ligroin it separated as a white solid, m.p. 85 to 92° C. Successive recrystallizations from water with treatment with Norite gradually raised the melting point to 130°. Found: C, 60.7; H, 7.00%; equivalent weight, 203. Calc. for  $C_{12}H_{14}O_4$ : C, 60.6; H, 7.07%; equivalent weight, 196.

The acid lactone was soluble in acetone, chloroform, benzene, ethyl acetate, acetic acid, and hot water, but it was sparingly stable in carbon tetrachloride and cold water and was insoluble in ligroin.



*2-Ketocyclohexylsuccinic Acid (VI)**(a) By Bromine-magnesium-hydroxide Oxidation*

Crude cyclohexanolsuccinic acid lactone (24 gm.) was dissolved in 5 *N* sodium hydroxide solution (103 cc.) by heating to boiling; the solution was stirred mechanically, while a hot solution of magnesium sulphate (61 gm. of the heptahydrate in 42 cc. of water) was slowly added. The flask was cooled below 10° C. by immersion in ice and the stirring continued while bromine (7 cc.) was dropped in slowly over a period of two hours. A fresh supply of ice was packed around the flask and it was allowed to resume room temperature by standing overnight. Next morning the solution was acidified with 10 *N* sulphuric acid (39 cc.) and the oily layer separated. The aqueous portion was evaporated on a sand-bath until evaporation of salts caused bumping. It was then extracted with ether, combined with the oil, and dried over anhydrous sodium sulphate. On removal of the ether, the crude keto acid was left as a syrup (25 gm.). This was purified by dissolving in hot benzene (40 cc.) and adding hot ligroin (25 cc.). The solid (21 gm.) that thus separated was crystallized three times from glacial acetic acid; the crystals, which were washed with a little chloroform, melted at 152°.

A simpler method of purification was to redissolve the crude syrupy acid in 5 *N* sodium hydroxide solution and boil with Norite. After filtration the clear solution was neutralized carefully with acid and evaporated to small volume. The keto acid was extracted with ether and recrystallized from a small volume of hot water. A 50% yield of pure keto acid melting at 154 to 155° was thus obtained. Found: C, 56.3; H, 6.56%; equivalent weight, 107.5 (indicating two carboxyl groups). Calc. for  $C_{10}H_{14}O_5$ : C, 56.1, H, 6.54%; equivalent weight, 107.

The keto acid was soluble in alcohol, ether, acetic acid, acetone, and water, sparingly soluble in benzene, and insoluble in chloroform and ligroin.

*(b) By Permanganate Oxidation*

Cyclohexanolsuccinic lactone (1 gm.) was dissolved in 5 *N* sodium hydroxide solution (10 cc.), and potassium permanganate solution (0.532 gm. in 10 cc. of water) was run in slowly. The temperature was not permitted to rise above 40 to 50° during the addition of the permanganate. When the permanganate was decolorized, the manganese dioxide that had precipitated was removed by filtration and the alkaline solution was boiled with Norite. The solution was neutralized with 10 *N* sulphuric acid (5 cc.), evaporated under reduced pressure, and the keto acid extracted with ether. On evaporation of the ether the crude acid remained; it was purified by crystallization from water. The crystals (0.53 gm.) melting at 151 to 153° were identical with those of the previous preparation.

*The Lactone of 2-Ketocyclohexylsuccinic Acid (2-Oxohexahydrobenzofuran-3-acetic Acid) (VII)*

Crude 2-ketocyclohexylsuccinic acid (5 gm.) was heated at 200° C. under reduced pressure for two hours. On cooling, when the temperature of the

material had fallen to about 100°, it was poured into benzene (15 cc.) from which it soon crystallized. The crude product (4.5 gm.) thus obtained was again crystallized from benzene (Norite). Colourless crystals, melting at 116 to 118° were thus obtained, which were soluble in alcohol, ether and water, sparingly soluble in cold benzene, and insoluble in ligroin. Found: C, 61.2; H, 6.10%; equivalent weight, 200. Calc. for  $C_{10}H_{12}O_4$ : C, 61.2; H, 6.12%; equivalent weight, 196.

*The Lactam of 2-Ketocyclohexylsuccinic Acid (2-Oxohexahydroindole-3-acetic Acid) (VII)*

Crude 2-ketocyclohexylsuccinic acid (4 gm.) was dissolved in 95% alcohol (10 cc.) in a pressure bottle and saturated with ammonia gas at 40° C. The bottle was then securely stoppered and set in a water-bath at 100° for four hours. When cool, the bottle was opened carefully, water (10 cc.) added, and 10 cc. of the solution was distilled. Another portion of water (10 cc.) was added and the solution was again distilled. A third portion of water was added and the distillation continued till the temperature reached 100°. The solution was boiled with charcoal and, after filtering, acidified with 10 *N* sulphuric acid (2 cc.). On cooling in ice, the lactam separated as a white solid (3.2 gm.). It was filtered off and washed well with water. The lactam, which melts at 201° C., was somewhat hygroscopic. It was soluble in acetic acid and alcohol, but only slightly soluble or insoluble in benzene, chloroform, ether, acetone, and water. Found: C, 61.7; H, 6.61; N, 7.24%; equivalent weight, 193. Calc. for  $C_{10}H_{13}O_3N$ : C, 61.5; H, 6.67; N, 7.18%; equivalent weight, 195. Kendall (9) purified his glutaric lactam by heating with charcoal in alkaline solution. However the succinic lactam evolved ammonia in alkaline solution (1.25 *N*) even in the cold, being less stable than the corresponding glutaric derivative. Analysis of the product which had been given this treatment showed that it contained less than 90% of the calculated amount of nitrogen.

*Lactone of Cyclohexanolacetic Acid (X)*

This was prepared by the method of Coffey (4); it boiled at 138 to 144°C. (16 mm.) or 137 to 140° (12 mm.). Yields of 63% theoretical on the basis of the cyclohexene oxide were obtained.

*2-Ketocyclohexylacetic Acid (XI)*

Cyclohexanolacetic lactone (28 gm.), 5 *N* sodium hydroxide solution (150 cc.), magnesium sulphate solution (87 gm. of the heptahydrate in 65 cc. of water), and bromine (11 cc.) were treated in the manner described above for the preparation of 2-ketocyclohexylsuccinic acid. The reddish brown oil (b.p. 150 to 180° C. (20 mm.)) obtained after removal of the ether was crystallized by cooling in ether and solid carbon dioxide. The solid keto acid was freed from the remaining oil as far as possible by filtration and was crystallized from hexane. A further recrystallization from hexane gave a white solid (11 gm.) melting at 73 to 74°. Found: C, 61.5; H, 7.41%; equivalent weight, 156. Calc. for  $C_8H_{12}O_3$ : C, 61.5; H, 7.69%; equivalent weight, 156. The

melting point of this keto acid as prepared by Chuang and Ma (3) is given as 39 to 41°, while the Indian workers (2, 7) give only boiling points. The sample prepared as above seems to be considerably purer than earlier specimens. We have prepared the semicarbazone melting at 199 to 200°; this melting point is in agreement with that found by Ghosh (7) and Chatterjee (2).

The reddish oil from which the crystals of the keto acid were separated proved to be unchanged cyclohexanolacetic lactone, as further quantities of the keto acid were obtained when the oil was again subjected to oxidation.

*The Lactone of 2-Ketocyclohexylacetic Acid (2-Oxohexahydrobenzofuran) (XII)*

2-Ketocyclohexylacetic acid (5 gm.) was heated under reduced pressure at 200° C. for two hours in an oil-bath. The lactone was purified by distillation; it boiled at 160 to 165° (25 mm.). Its melting point was 7 to 8°. The lactone was insoluble in water, but soluble in alcohol, ether, acetone, and benzene. Found: C, 69.4; H, 7.39%. Calc. for  $C_8H_{10}O_2$ : C, 69.6; H, 7.25%. The lactone ring was readily opened by hot *N*/10 sodium hydroxide solution.

*Attempted Preparation of the Lactam of 2-Ketocyclohexylacetic Acid*

Crude 2-ketocyclohexylacetic acid (20 gm.) was treated with alcoholic ammonia in a pressure bottle, as previously described. When cool, the alcohol and ammonia were removed under reduced pressure on a steam-bath and the thick amber residual oil distilled *in vacuo*. Fraction I, boiling at 178 to 182° (10 mm.), consisted of nearly pure unchanged keto acid. Fraction II, boiling at 182 to 198° (10 mm.), was quite viscous and quite red in colour. This viscous red oil gave a strong qualitative test for nitrogen, but it could not be induced to crystallize. It was soluble in water, alcohol, acetone, and benzene, but insoluble in ligroin.

*2-Ketocyclohexylmalonic Acid (XIV)*

The lactone of  $\alpha$ -carbethoxycyclohexanolacetic acid (IX) was prepared from cyclohexene oxide according to the directions of Coffey (4). The fraction used distilled at 190 to 200° C. (10 mm.).

The ester-lactone (28 gm.) mixed with 5 *N* sodium hydroxide (103 cc.) and sufficient alcohol to give a clear solution was hydrolyzed by boiling under the reflux condenser. The alcohol was removed under reduced pressure and to the mechanically stirred hot solution magnesium sulphate solution (61 gm. of the heptahydrate in 42 cc. of water) was run in slowly. To prevent the solution setting to a gel a further quantity of water (50 cc.) was necessary at this stage. The oxidation with bromine (7 cc.) then proceeded in the usual manner with the exception that the solution was evaporated while still alkaline. On evaporation of the ether a reddish oil (10 gm.) remained from which crystals (2 gm.) of the keto acid separated. These were washed with chloroform and recrystallized from acetic acid, melting at 163° C. with decomposition. Found: C, 54.2; H, 6.18%; equivalent weight, 99.5. Calc. for  $C_9H_{12}O_5$ : C, 54.0; H, 6.00%; equivalent weight, 100. The keto acid was soluble in alcohol, acetone, acetic acid, ether, and water, but insoluble in chloroform, benzene and ligroin.

A semicarbazone was prepared, but it was found to be quite soluble, and insufficient for analysis was obtained. It melted with decomposition at 271°.

2-Ketocyclohexylmalonic acid was also produced from the ester lactone (IX) by oxidation with permanganate in the manner previously described for 2-ketocyclohexylsuccinic acid. A yellow oil was obtained which on standing gave some crystals of the keto acid, but not so pure as those produced by the bromine-magnesium-hydroxide method. On further standing this oil deposited a second crop of crystals, which, on recrystallization from acetic acid, melted at 121 to 122° C. These proved to be the lactone of cyclohexanolmalonic acid (XIII), which Coffey (4) prepared although never in the solid condition. Found: C, 58.7; H, 6.70%; equivalent weight, 182. Calc. for  $C_9H_{12}O_4$ : C, 58.7; H, 6.52%; equivalent weight, 184.

*Attempted Preparation of the Lactam of 2-Ketocyclohexylmalonic Acid*

Efforts to isolate this lactam, prepared according to the procedure already described, were unsuccessful, no doubt owing in part to its considerable solubility in water. However, when the reaction mixture was evaporated to small volume under reduced pressure and extracted with ether-alcohol, a nitrogenous oil was obtained which could not be induced to crystallize. The oil was unstable and lost ammonia readily. It resembled the product made similarly from 2-ketocyclohexylacetic acid and may in fact be identical with it. This was supported through the examination of a crystalline sublimate found in the cooler portion of the pressure bottle. This material sublimed rapidly at 135° to 140° C. and was found to contain 21.8% nitrogen. The material is probably related to ammonium carbonate or carbamate, since it was found that when ammonium carbonate and alcoholic ammonia were heated together under the same conditions as used for lactam formation a sublimate of somewhat similar properties was obtained although of somewhat higher but varying nitrogen content, thus pointing to decarboxylation of the malonic acid as the source of the carbon dioxide required for the formation of the former sublimate. At all events it is unlikely on account of its high percentage of nitrogen that it is related to the desired lactam since even the amide-lactam of 2-ketocyclohexylmalonic acid would have a content of but 15.6% nitrogen.

*The Lactone of Cyclohexanolbenzylacetic Acid (XV)*

Sodium (7.5 gm.), absolute alcohol (125 cc.), ethyl malonate (50 gm.), cyclohexene oxide (30 gm.), and benzyl chloride (75 gm.) were treated according to the directions given for the preparation of the lactone of cyclohexanolsuccinic acid. As no reaction occurred with the benzyl chloride at room temperature, the benzene suspension was refluxed for 35 hr. on the steam-bath. A steam distillation was necessary to remove final traces of unreacted benzyl chloride. After saponification on acidification the unpleasant smelling acid lactone rose to the surface as an oil and was separated. It was decarboxylated by heating to 220° C. in an oil-bath. The residue was dissolved in ether and dried. On evaporation of the ether, the lactone was left as an

almost colourless, viscous oil (32 gm.). It was purified by distillation, boiling at 202 to 204° (10 mm.). Found: C, 78.0; H, 7.92%. Calc. for  $C_{15}H_{16}O_2$ : C, 78.3; H, 7.83%. The lactone was soluble in alcohol, ether, and acetic acid, but insoluble in water, ligroin and chloroform.

*2-Ketocyclohexylbenzylacetic Acid (XVI)*

Cyclohexanolbenzylacetic lactone (30 gm.), 5 *N* sodium hydroxide solution (114 cc.), magnesium sulphate solution (66.6 gm. of the heptahydrate in 47 cc. water), and bromine (7.4 cc.) were treated in the manner previously described. In this case it was found necessary to add a little alcohol and reflux in order to open the lactone ring. The alcohol was then removed and the oxidation carried on in the normal manner. When the solution was neutralized with 10 *N* sulphuric acid the keto acid rose to the surface as an oil. The crude acid distilled at 197 to 225° C. (3 mm.). On redistillation two fractions were collected; I, boiling at 172 to 185° (3 mm.), and II, boiling at 185 to 195° (3 mm.). When either of these fractions was redistilled, the boiling point rose gradually during the process and the hot distillate lost the green tint that had been quite noticeable during the first distillation. These distillates also decolorized bromine water and permanganate, whereas the undistilled keto acid did not. The conclusion was that the keto acid was losing a molecule of water during the distillation, with the formation of the unsaturated lactone. All the distillates were heated for three hours at 200° *in vacuo* to complete the change to the lactone. On distillation, the lactone (5 gm.) was obtained boiling at 220 to 240° (16 mm.). Found: C, 78.3; H, 6.69%. Calc. for  $C_{15}H_{16}O_2$ : C, 78.9; H, 7.02%. Attempts to produce the keto acid by opening the lactone ring and to form a solid lactam have so far been unsuccessful.

*The  $\gamma$ -Lactone of Cyclohexanol- $\alpha$ -propionic Acid (XVII)*

Sodium (9.1 gm.), absolute alcohol (155 cc.), ethyl malonate (63 gm.), and cyclohexene oxide (38 gm.) were treated in the manner previously described. Methyl iodide (55 gm.) was added to the benzene suspension of the sodio-diester and refluxed on the water-bath for 20 hr. Following saponification and decarboxylation in the usual manner the lactone was isolated as a colourless oil (26 gm.) boiling at 148 to 150° C. (21 mm.). Found: C, 69.8; H, 9.54%. Calc. for  $C_9H_{14}O_3$ : C, 70.1; H, 9.09%.

*2-Ketocyclohexyl- $\alpha$ -propionic Acid (XVIII)*

The lactone of cyclohexanol- $\alpha$ -propionic acid (25 gm.) was oxidized in the usual manner with bromine and magnesium hydroxide. The oily layer that formed on acidification was separated; it soon solidified. The solid was crystallized from hot benzene (charcoal) by the addition of ligroin. After two more recrystallizations in the same manner it was obtained as a white solid (5 gm.), m.p. 133 to 135° C. Found: C, 63.10; H, 8.6%; equivalent weight, 168. Calc. for  $C_9H_{14}O_3$ : C, 63.53; H, 8.23%; equivalent weight, 170.

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## THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXXV. *CORYDALIS PLATYCARPA* MAKINO<sup>1</sup>BY RICHARD H. F. MANSKE<sup>2</sup>

## Abstract

*Corydalis platycarpa* Makino has yielded nine alkaloids as follows,—protopine, *l*-isocorypalmine, isocorydine, corybulbine, aurotensine, *l*-tetrahydro-palmatine, corydaline, bicuculline, and *dl*-stylopine. No new alkaloids were found but a small amount of a neutral nitrogenous substance,  $C_8H_9ON$ , was obtained. The alkaloid previously termed luteanine was found to be identical with isocorydine.

In appearance and habit *Corydalis platycarpa* Makino, a native of Japan, closely resembles *C. pallida* (Thunb.) Pers. It is however a more robust plant, and emits a very unpleasant and persistent odour particularly when bruised. The substance responsible for this odour was not isolated. The odour does not persist in the dried plant.

The nature of the contained alkaloids presents no features of unusual interest, It is noteworthy however that capaurine was not found. It is becoming clear that only some species in the Section *Eucorydalis* Prantl, Subsection *Eucapnoides* Fedde, of the genus *Corydalis* contain this alkaloid, and its absence may indicate a more remote relationship than taxonomy admits.

The following six plants in this subsection have been examined by the author,—*C. sempervirens* (3), *C. aurea* (4), *C. micrantha* (5), *C. crystallina* (5), *C. pallida* (8), and *C. montana* (9). It is more than probable that the absence of capaurine from two of these, namely, *C. sempervirens* and *C. crystallina*, is indicative of a distinction not admitted by botanists.

The plant under investigation has yielded protopine, *l*-isocorypalmine, isocorydine, corybulbine, aurotensine, *l*-tetrahydro-palmatine, corydaline, bicuculline, and *dl*-stylopine. This isolation of corybulbine is the first in the author's experience during which nearly thirty fumariaceous plants have been examined. The presence of isocorydine calls for some comment. Its presence in the genus *Corydalis* is rare, but the author has recorded it as occurring in *C. lutea* (6). Unfortunately the latter plant was stated to contain a new alkaloid which was named luteanine. This base has now been shown to be isocorydine. The same error was committed during an examination of *Glaucium flavum* (7). It has been observed that, although isocorydine is phenolic, it is only sparingly soluble in aqueous alkali and when much is present an appreciable amount of it is precipitated along with the non-phenolic bases. It becomes necessary therefore to reverse the former conclusion that *G. serpyteri* Heldr. is entitled to specific rank (10), and retain for it a varietal designation (of *G. flavum*).

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<sup>2</sup> Chemist.

Virtually all of the basic material was ultimately obtained in crystalline form. It is concluded therefore that any other alkaloids that may have been present constituted only an insignificant fraction of the whole. There was obtained, however, a neutral nitrogenous compound and it is probable that only a small amount of that present was actually isolated. The fraction LC (2) contained much fumaric acid and it is likely that most of the new substance was lost when this fraction was discarded. Analytical figures point to the formula,  $C_6H_9ON$ , methoxyl and N-methyl groups being absent. It is oxidized instantly by permanganate in aqueous solution and catalytic hydrogenation yields a non-crystalline volatile substance. There was not sufficient material for a thorough examination, but it was shown to be different from the amide of sorbic acid, which melts at the same temperature and with which it is isomeric.

### Experimental

The material for this investigation was grown in a local garden, and consisted almost entirely of the first year's growth. The plant is a facultative biennial that is not entirely winter hardy in this climate. The dried and ground material weighed 5.8 kg., of which the roots constituted 230 gm. The entire material was worked up in one operation. The following is a summary of the various fractions and the contained alkaloids (2).

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,— *l*-tetrahydro-palmatine, corydaline, bicuculline, *dl*-stylopine.

EC—Phenolic bases extracted from alkaline solution by means of chloroform,—corybulbine, isocorydine.

BCE and EEC—Phenolic bases precipitated by carbon dioxide,—*l*-isocorypalmine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—protopine.

BSE and EES—Phenolic bases precipitated by carbon dioxide,—aurotensine.

#### *l*-Tetrahydro-palmatine

The non-phenolic fraction (BC) was redissolved in hot dilute hydrochloric acid. The filtered solution deposited a sparingly soluble hydrochloride from which the free base was regenerated. When recrystallized from hot methanol it melted at 142° C.\* and in admixture with a specimen of *l*-tetrahydro-palmatine it melted at the same temperature, but when admixed with *d*-tetrahydro-palmatine it melted indefinitely at 138 to 140° C. The yield was about 4.2 gm.

#### Corydaline

The filtrate from the separation of the above *l*-tetrahydro-palmatine hydrochloride was basified with ammonia, extracted with much ether, and the washed extract evaporated. The residue in contact with methanol deposited a few crystals of protopine and then the characteristic polyhedra of corydaline.

\* Melting points are corrected.



When recrystallized once from methanol the latter melted either alone or in admixture with corydaline at 135° C. The yield was about 0.6 gm.

*Bicuculline and dl-Stylopine*

The methanolic filtrate from which the corydaline had crystallized was redissolved in dilute acid and the bases were recovered by addition of ammonia and extraction with ether. The residue from the latter in contact with methanol then deposited a mixture of bases that was extracted with several successive portions of hot methanol, which removed a small amount of corydaline. The sparingly soluble portion was recrystallized from chloroform-methanol. A mixture of two bases, fine needles and stout rectangular plates, was obtained. The latter melted sharply at 177° C. either alone or in admixture with bicuculline. The melt resolidified and then remelted at 193 to 195° C. This mixture was separated by heating with methanol and adding chloroform in small quantities until the bicuculline had dissolved. The residual base was then recrystallized from chloroform-methanol and melted at 220° C. When mixed with *dl*-stylopine it melted at 220 to 221° C. The yield of each of these bases was somewhat less than 50 mg.

*Corybulbine*

The fraction (EC) crystallized for the greater part as the ether was evaporated. The dry residue was washed with a little cold ether and then heated with methanol. The undissolved base was recrystallized from chloroform-methanol. It was obtained in brilliant colourless stout prisms that melted at 234° C. when rapidly heated. There was however appreciable previous darkening and sintering, but in an evacuated tube the base melted sharply and without discoloration at 244° C. When admixed with a specimen of corybulbine kindly supplied by Prof. K. Brandt of the University of Marburg, Germany, it also melted at 244° C. *in vacuo*. Calc. for  $C_{21}H_{25}O_4N$ : 3 OMe, 26.19%. Found: OMe, 25.65, 25.62%.

A small portion suspended in methanol was methylated with diazomethane. The non-phenolic base isolated in the usual way was identical with corydaline (melting point and mixed melting point). The yield of corybulbine was about 0.1 gm.

*Neutral Compound,  $C_6H_9ON$*

The methanol extract from the corybulbine was concentrated to a small volume and the substance that then separated was recrystallized three times from hot methanol, in which it is moderately soluble. The colourless rectangular plates thus obtained melted sharply at 172° C. The substance dissolved in sulphuric acid to yield a colourless solution that remained colourless on heating to a high temperature. Found: C, 64.54, 64.88; H, 8.27, 8.28; N, 12.62%; mol. wt., 133, 134 (Rast). Calc. for  $C_6H_9ON$ : C, 64.87; H, 8.11; N, 12.61%; mol. wt., 111. Methoxyl and N-methyl groups were absent. In admixture with sorbamide (1) melting at 172° C. it was completely liquid at 150° C. It dissolved readily in water and the solution decolorized permanganate instantly.

### *Isocorydine*

The methanolic solution from which the above neutral nitrogenous compound had crystallized was evaporated and the residue dissolved in dilute acid. The filtered solution was basified with ammonia, extracted with ether, and the ether evaporated. The residue in contact with methanol yielded a base which, when recrystallized twice from methanol, was obtained in pale yellow prisms melting at 185° C. either alone or in admixture with isocorydine.

### *l-Isocorypalmine*

The fractions (BCE and EEC) were isolated together by extracting the carbonated solution with successive portions of ether. The residue from the ether solution in contact with methanol deposited a sparingly soluble base, which was recrystallized from chloroform-methanol. It then consisted of colourless stout prisms melting at 230° C. in an open tube or at 241° C. (*in vacuo*). A mixture of this base with a specimen of *l*-isocorypalmine from *C. lutea* melted at the same respective temperatures. The yield was about 0.2 gm.

The filtrate from the above deposited a small amount of corybulbine and on concentration a small amount of isocorydine was obtained.

### *Protopine*

The non-phenolic fraction (BS) was dried, dissolved in chloroform, and the filtered solution evaporated to a thin resin. The resin was dissolved in hot methanol and the solution was seeded with a nucleus of protopine. The base, which then crystallized, melted at 210° C. either alone or in admixture with an authentic specimen of protopine. The yield was 3.1 gm. Attempts to isolate other bases from the mother liquor failed.

### *Aurotensine*

The bases in fractions (BSE and EES) were isolated by exhaustive extraction with ether. The residue from the extract was converted into hydrochloride in methanol, and the sparingly soluble hydrochloride thus obtained converted to free base, which was recrystallized from methanol. The pale pink four sided plates of aurotensine thus obtained melted sharply at 128° C. either alone or in admixture with an authentic specimen. The yield was 50 mg.

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AN ALKALOID FROM *MENISPERMUM CANADENSE* L.<sup>1</sup>BY RICHARD H. F. MANSKE<sup>2</sup>

## Abstract

The chief and perhaps the only alkaloid of *Menispermum canadense* L. has been shown to be identical with dauricine, an alkaloid from *M. dauricum* D.C.

*Menispermum canadense* L. is a woody liana widely but not abundantly distributed throughout eastern North America. There is no record of an adequate chemical examination. Gordin (1) confined himself to the negative assertion that berberine is not present in the plant.

The present investigation was undertaken to determine the nature of the contained alkaloid or alkaloids. A preliminary examination disclosed that the leaves were virtually free of alkaloids and that the aerial stems contained only minute amounts. The subterranean stems and the roots were found to contain 2.2% of total alkaloid.

All attempts to obtain a crystalline base or a crystalline salt failed, and no indication was obtained that more than one alkaloid is present in the plant. The purest specimen consisted of a pale yellowish resin soluble without turbidity in methanol, chloroform, dilute acid, or dilute sodium hydroxide, the last observation indicating the presence of a phenolic hydroxyl. The base was easily methylated with diazomethane in methanol and the now completely non-phenolic base was obtained only as a colourless resin. This difficulty of obtaining a crystalline product is characteristic of the alkaloid dauricine, an alkaloid occurring in *Menispermum dauricum* D.C. (2). That the alkaloid from *M. canadense* is dauricine was rendered probable by the fact that its dimethiodide corresponded closely in melting point and optical activity with that of dauricine. An authentic specimen of the latter was not available for direct comparison so that the alkaloid was degraded by Hofmann's method and oxidation to its ultimate fragments, namely *m*-hemipinic acid and 4-methoxy-3 : 4'-diphenyl-ether-1 : 1'-dicarboxylic acid. These are the products obtained by Kondo and co-workers (3, 4) from dauricine. There remained the determination of the position of the free hydroxyl group. When the complete degradation was carried out with the O-ethyl ether there was obtained 4-ethoxy-3 : 4'-diphenyl-ether-1 : 1'-dicarboxylic acid as well as *m*-hemipinic acid. It is therefore concluded that the alkaloid of *M. canadense* is dauricine.

## Experimental

*Isolation and Purification of the Alkaloid*

The material was collected in a shady damp grove near the Rideau River in June. The washed, dried, and ground subterranean portion weighed 6.3

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kg. It was extracted with methanol in Soxhlet apparatus and the extract largely freed of the solvent. The residue was acidified with hydrochloric acid, diluted with five litres of hot water, and heated until the methanol was expelled. The mixture was set aside for several weeks, during which time the resins formed a coherent mass. The clear aqueous solution was decanted through a charcoal filter, and exhausted with ether. It was then basified with excess ammonia and the precipitated alkaloid extracted with chloroform. The residue from the chloroform extract was redissolved in dilute hydrochloric acid and the filtered solution treated with a large excess of aqueous sodium hydroxide solution. The precipitated base first redissolved in the slight excess of sodium hydroxide and then reprecipitated as a sparingly soluble resinous sodium salt. After standing overnight the clear supernatant aqueous solution was decanted from the precipitate (only a small amount of alkaloid remained in this solution). The precipitate was then redissolved in water, filtered through a layer of charcoal to remove a slight turbidity, and then saturated with a stream of carbon dioxide. The base was thus precipitated in a finely granular form that could be easily filtered and washed. After drying, it weighed 138 gm. (2.2%).

As thus prepared, dauricine was only sparingly soluble in ether but it dissolved readily and completely in methanol, chloroform, dilute acid, or dilute sodium hydroxide.

The dimethiodide crystallized readily when a dilute methanolic solution of the alkaloid was treated with an excess of methyl iodide. It was recrystallized four times from hot methanol, and it then consisted of fine colourless needles melting sharply at  $201^{\circ}\text{C}.$ ;  $[\alpha]_{\text{D}}^{20} - 114^{\circ}$  ( $c = 0.3484$  in water). Dauricine dimethiodide is stated to melt at  $204^{\circ}$  and  $[\alpha]_{\text{D}}^{22}$  is given as  $-110^{\circ}$ .

#### *Degradation of Dauricine*

A methanolic solution of the base was treated with an excess of an ethereal solution of diazomethane, the solvents were removed after 24 hr., and the residue was dissolved in dilute hydrochloric acid. The filtered solution was basified with an excess of sodium hydroxide and the liberated base extracted with ether. The resulting non-phenolic base (dauricine O-methyl ether) was dissolved in methanol and treated with methyl iodide. The methiodide was dissolved in water and heated on the steam-bath with an excess of potassium hydroxide. The methine base, which slowly separated, was removed at intervals by extraction with ether. The residue from the combined ether extracts was redissolved in dilute acid, the filtered solution basified with sodium hydroxide, and the liberated base re-extracted with ether. The colourless resinous product was dissolved in methanol and treated with methyl iodide. The oily dimethine dimethiodide crystallized for the greater part in

\* All melting points are corrected.

the course of several days. A portion was first recrystallized from a mixture of chloroform and methanol. It was then dissolved in hot water, in which it is readily soluble, evaporated to a small volume, and treated with a large volume of methanol. The still warm solution then deposited the dimethiodide in colourless needles, which, when washed with methanol and dried, melted at 211° C. Found: C, 53.56, 53.52; H, 5.90, 6.00; N, 2.60; OMe, 15.80, 16.03; I, 25.63%. Calc. for  $C_{42}H_{50}O_6N_2 \cdot 2CH_3I \cdot H_2O$ : C, 53.43; H, 6.00; N, 2.90; 5 OMe, 16.05; I, 26.28%.

The crude dimethine dimethiodide was dissolved in hot water and heated on the steam-bath with sodium hydroxide (trimethylamine, identified as its platinichloride, was copiously given off). At intervals the liberated unsaturated hydrocarbon was extracted with chloroform. It was then dissolved in acetone containing a little water and treated with powdered potassium permanganate until the colour of the latter remained for 24 hr. Methanol was added to destroy the excess permanganate, the mixture was diluted with water, boiled until free of acetone, filtered, and the filtrate acidified with excess hydrochloric acid.

The sparingly soluble acid which crystallized from the warm solution was filtered off and recrystallized from a large volume of boiling methanol. It was obtained in greyish needles, which melted at 308° C. Späth and Pikel (5) give the melting point of 4-methoxy-3 : 4'-diphenylether-1 : 1'-dicarboxylic acid as 313 to 314° C. (*in vacuo*). Found: C, 62.97; H, 4.58; OMe, 11.05%. Calc. for  $C_{18}H_{12}O_6$ : C, 62.50; H, 4.16; OMe, 10.76%.

The dimethyl ester was prepared in methanol by the action of diazomethane. It was distilled *in vacuo* (b.p., 180° C. (0.03 mm.)) and then recrystallized from methanol; m.p., 97° C. Späth and Pikel give m.p., 97 to 98° C. Found: C, 64.52; H, 5.00; OMe, 29.47%. Calc. for  $C_{17}H_{16}O_6$ : C, 64.56; H, 5.06; 3 OMe, 29.43%.

The aqueous acid solution from which the above acid had been precipitated was exhausted with ether and the residue triturated with water. A small amount of the sparingly soluble diphenylether acid was removed by filtration and a small amount of oxalic acid was removed by adding a solution of calcium acetate. The clear aqueous solution was then acidified with hydrochloric acid and again exhausted with ether. The residue from the ether was recrystallized from a small volume of water. The colourless prisms thus obtained melted at 187° C. either alone or in admixture with an authentic specimen of *m*-hemipinic acid. The *N*-ethyl-imide was sublimed *in vacuo* and recrystallized from methanol. Either alone, or in admixture with an authentic specimen of *N*-ethyl-*m*-hemipinimide, it melted sharply at 233° C.

The *O*-ethylation and subsequent degradation of the alkaloid were carried out exactly as with the *O*-methylation product. No attempt was made to

isolate crystalline intermediates. The water soluble acid was shown to be *m*-hemipinic acid by conversion to its N-ethyl-imide. The water insoluble acid was first recrystallized from methanol and then from phenol. It was obtained in almost colourless fine needles melting sharply at 286° C. Kondo and co-workers give the melting point of 4-ethoxy-3 : 4'-diphenylether-1 : 1'-dicarboxylic acid as 276 to 277° C. (presumably uncorrected) and Späth and Pikl record 288 to 289° C.

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